

REGIOSELECTIVE THERMOLYSIS OF 1,4-DIPHENYLBUTANE  
ENHANCED BY RESTRICTED RADICAL MOBILITY

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INTRODUCTION

Thermal decomposition of coal has been postulated to involve the formation of free radicals by processes such as the homolysis of aliphatic or ether-containing bridges which connect polycyclic aromatic units into a macromolecular structure.<sup>1</sup> Understanding the thermal reactivity of coal is important in the study of pyrolysis, liquefaction, and coking.<sup>2</sup> Mechanistic insights into the chemical reactivity of coal at the molecular level can be gained from the study of model compounds which represent structural features in coal. However, radicals generated in a cross-linked macromolecular material such as coal may experience restricted mobility when the radical center remains bound to the residual molecular structure. To model the effects of restricted radical mobility on thermally induced decomposition reactions, thermolyses of model compounds covalently attached to an inert support have been studied. Thermolysis of surface-immobilized 1,2-diphenylethane showed a substantially altered free radical reaction pathway compared with the corresponding liquid phase behavior,<sup>3</sup> while thermolysis of surface-immobilized 1,3-diphenylpropane (~~DPP) showed unexpected regioselectivity resulting from conformational restrictions on hydrogen transfer reactions as the surface coverage of ~~DPP decreased.<sup>4</sup> In order to further explore the regioselectivity of hydrogen transfer induced by restricted diffusion, the thermolysis of surface-immobilized 1,4-diphenylbutane (~~DPB) is being examined.

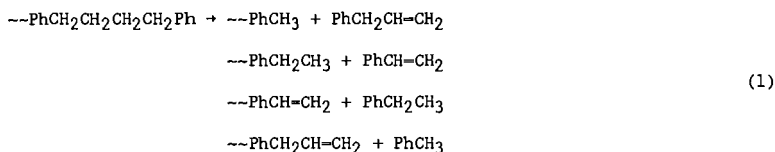
EXPERIMENTAL

*p*-(4-phenylbutyl)phenol (HODPB) was prepared in a four-step synthesis from the Wittig reaction of cinnamyltriphenylphosphonium chloride with *p*-anisaldehyde to afford 1-(4-methoxyphenyl)-4-phenyl-1,3-butadiene which was catalytically reduced (10% Pd/C) and demethylated (HBr/HOAc). Repeated crystallizations from hexanes afforded HODPB in >99.9% purity (GC). Surface-immobilized 1,4-diphenylbutane was prepared at saturation coverage by condensation of excess HODPB with the surface hydroxyls of a high purity fumed silica (Cab-O-Sil, M-5, Cabot Corp., 200 m<sup>2</sup>/g) at 225°C for 1 h, as previously described.<sup>3</sup> Excess phenol was sublimed from the Cab-O-Sil by heating at 270°C for 45 min under vacuum ( $5 \times 10^{-3}$  Torr). Following base hydrolysis of the Cab-O-Sil (to liberate surface-bound phenol) and silylation, GC analysis gave coverages for three different batches as 0.504, 0.548, and 0.541 mmol of ~~DPB per gram of final product with a purity >99.7%.

Thermolysis of ~~DPB was performed at  $400 \pm 1^\circ\text{C}$  in T-shaped pyrex tubes sealed under high vacuum ( $\approx 10^{-6}$  Torr). The volatile products were collected in a cold trap while the surface-bound products were removed from the silica as the corresponding phenols by basic digestion and then silylated to form trimethylsilyl ethers. The samples were analyzed by capillary GC with flame ionization detection or by GC-MS. Quantitative measurements were made with the use of internal standards and measured GC detector response factors.

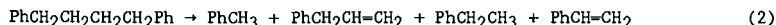
## RESULTS AND DISCUSSION

Thermolysis of  $\sim\sim$ DPB at 400°C has been studied at 2-12% conversion with two high coverage batches, 0.541 mmol/g (Batch A) and 0.504 mmol/g (Batch B). At the lowest conversion (ca. 2% in 10 min), the major gas phase products of the cracking reaction detected in the cold trap were toluene (PhMe), ethylbenzene (PhEt), styrene (PhVi), and allylbenzene (PhAlI). The surface-attached products obtained as phenols from basic digestion of the sample were *p*-cresol (corresponding to  $\sim\sim$ PhMe), *p*-ethylphenol ( $\sim\sim$ PhEt), *p*-hydroxystyrene ( $\sim\sim$ PhVi), and *p*-hydroxyallylbenzene ( $\sim\sim$ PhAlI). These eight products (shown in eq. 1) account for >97% of the products formed at 2% conversion and 93% at 12% conversion. The product distribution for the four gas phase hydrocarbon products, which will be examined in more detail below, is shown as a function of conversion in Figure 1. The two high coverage batches gave similar product distributions with reaction rates slightly faster for Batch B (ca. 15%).



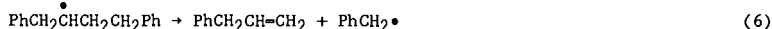
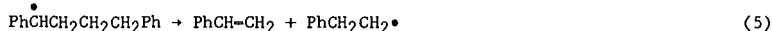
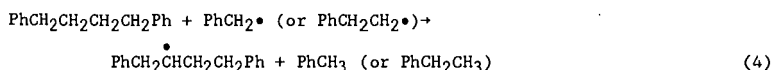
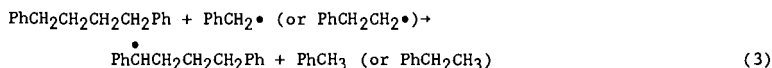
As conversion of  $\sim\sim$ DPB increased, secondary products formed at the expense of the surface-bound olefinic products. At the highest conversion studied (12%), 7.0 mol% of the products results from secondary reactions. The major secondary reactions appear to be rearrangement of  $\sim\sim\text{PhCH}_2\text{CH}=\text{CH}_2$  to  $\sim\sim\text{PhCH}=\text{CHCH}_3$  (2.6 mol %), and radical addition to  $\sim\sim\text{PhVi}$  and  $\sim\sim\text{PhAlI}$  to produce, following hydrogen abstraction,  $\sim\sim\text{PhCH}_2\text{CH}_2\text{CH}_2\text{Ph}$  (0.6 mol %),  $\sim\sim\text{PhCH}_2\text{CH}_2\text{CH}_2\text{Ph}\sim\sim$  (0.7 mol %; identified as the corresponding diphenol),  $\sim\sim\text{PhCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}\sim\sim$  (0.5 mol %), and isomers of  $\sim\sim\text{C}_{24}\text{H}_{24}\sim\sim$  (1.0 mol %; diphenols of triphenylhexane). Comparable secondary radical addition reactions have been reported to occur during thermolysis of liquid DPB.<sup>5</sup>

Thermolysis of liquid 1,4-diphenylbutane (DPB) has been shown to proceed by a radical chain decomposition reaction in which DPB is cracked to give four major products, as shown in equation 2.<sup>5</sup>

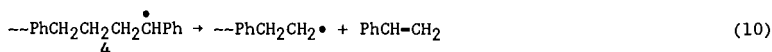
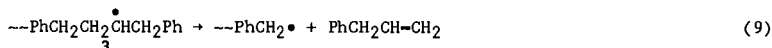
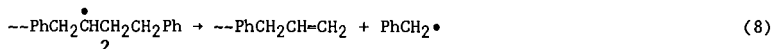
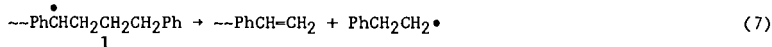


By comparison, surface-immobilized DPB reacted to form the same set of gas phase products as well as a corresponding set of surface-attached products (eq. 1). This results from the nonequivalence of the two ends of the surface-attached DPB molecule. Therefore, at low conversion, liquid DPB and  $\sim\sim$ DPB react in an analogous manner to produce the same slate of products. The initial rate of  $\sim\sim$ DPB thermolysis at high coverage ( $15 \pm 2\% \text{ h}^{-1}$  at 400°C based on 2-12% conversion) is somewhat faster than that of liquid DPB. Comparison of the rate of reaction of liquid DPB and  $\sim\sim$ DPB at 400°C for 10 min shows that the surface-immobilized DPB reacts 10-fold faster. It is also interesting that while the rate of decomposition of liquid DPB exhibited a mildly autocatalytic behavior, the rate of  $\sim\sim$ DPB decomposition calculated at each time point was independent of conversion. Additional studies will probe these observations further and examine the dependence of the thermolysis rate on surface coverage.

In the radical chain propagation steps for the decomposition of DPB, a benzyl radical (or a 2-phenylethyl radical) abstracts a hydrogen atom from DPB in a competitive process to form a benzylic and a nonbenzylic diphenylbutyl radical (eqs. 3 and 4). The  $\beta$ -scission of the benzylic radical leads to PhVi and ultimately PhEt, while the nonbenzylic radical leads to PhAlI and ultimately PhMe (eqs. 5 and 6).

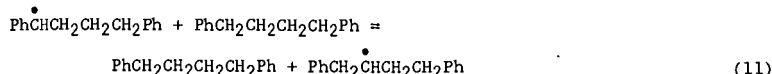


In the case of  $\sim\sim$ DPB, there are four different methylene units which can form two distinct benzylic (1 and 4) and two distinct nonbenzylic (2 and 3) radicals. Following initiation by the homolysis of a small amount of  $\sim\sim$ DPB, the  $\beta$ -scission steps of the four possible radicals formed by hydrogen abstraction are shown in equations 7-10.



The free and surface-bound radicals can propagate the chain by reacting with  $\sim\sim$ DPB to form free and surface-bound PhMe and PhEt while regenerating the surface-bound DPB radicals.

The regioselectivity for thermolysis of fluid phase DPB was found to be concentration dependent.<sup>5</sup> This was explained by a substrate-dependent hydrogen abstraction reaction which interconverts the benzylic and the nonbenzylic radicals, equation 11.



In the neat liquid at 400°C, conditions under which the reaction in eq. 11 occurs efficiently, the regioselectivity of thermolysis as determined from the PhEt/PhMe ratio extrapolated to zero conversion, was a minimum of 1.22. Interestingly for  $\sim\sim$ DPB at 400°C, the analogous regioselectivity for formation of 1 relative to 2, determined from the PhEt/PhMe ratio, at 2% conversion is 1.23, while the benzylic/nonbenzylic selectivity for the pair farthest from the surface (4 relative

to 3), determined from the PhVi/PhAlI ratio, is a somewhat smaller value of 1.08. These observations suggest that hydrogen exchange reactions on the surface analogous to eq. 11 may also be important for surface-immobilized --DPB at high coverage.

The selectivity for formation of benzylic radicals 4 and 1 can be probed by the PhVi to PhEt yield ratio since these products are not consumed by secondary reactions. At low conversions (2%), the ratio has a value of 1.0 indicating no selectivity, but as the conversion increases, the ratio increases to 1.2 at 12% conversion. A similar type of conversion dependent selectivity for the benzylic radical farthest from the surface has been reported in the thermolysis of --DPP at saturation coverages in which the selectivity varied from 1.0 at <4% conversion to 1.3 at 23% conversion. The explanation for this conversion dependent regioselectivity for --DPB lies in the hydrogen transfer propagation step. As the conversion increases, --DPB molecules are increasingly separated from the surface-bound hydrogen abstracting benzylic and 2-phenylethyl radicals, and hydrogen abstraction at the benzylic carbon farthest from the surface to form radical 4 becomes favored. Additional insight into this regioselectivity should be obtained from the current studies being performed at lower surface coverages.

#### CONCLUSIONS

Covalent attachment of organics to an inert support has proven useful in modeling the effects of the restricted radical mobility in the thermal reactions of coal related model compounds. Thermolysis of surface-immobilized 1,4-diphenylbutane at 400°C was found to proceed through a facile free radical chain decay pathway giving products analogous to those found in the thermolysis of liquid DPB, but with a somewhat faster rate. For --DPB at low conversions, there is little regioselectivity between the four radical chain decay pathways which cycle through radicals at benzylic and nonbenzylic methylene sites suggesting that a hydrogen exchange reaction may be important at high surfaces coverages. At the highest conversion studied (12%), the cracking favors hydrogen abstraction from the benzylic carbon farthest from the surface. Additional studies are in progress to examine the effects of lower surface coverages on the regioselectivity and rate of the thermal cracking of --DPB. The results from thermolysis of --DPP and --DPB support the idea that a free radical chain induced decomposition reaction can be an effective mechanism for the mild thermal degradation of polymethylene chains connecting aromatic moieties in coal even under conditions of restricted diffusion.

#### ACKNOWLEDGMENTS

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Figure 1. Thermolysis of  $\sim\text{Ph}(\text{CH}_2)_4\text{Ph}$

